Thermodynamic Modeling of the CaO-SiO_2-M_2O (M=K,Na) systems

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Abstract: The aim of the present study is the CALPHAD modeling of the systems CaO-SiO_2-M_2O (M=K, Na) based on a careful review of the available literature data – phase diagram and thermodynamics – as well as own experiments. The heat capacities (Cp) of three compounds, $CaSiO_3$, $K_2Ca_2Si_2O_7$ and $K_8CaSi_{10}O_{25}$, (determined using drop calorimetry) were included in the optimization of the ternary phase diagram CaO-SiO_2-K_2O.

Key words: Thermodynamics, Phase diagram, Modeling, Molten slag

1. Introduction

The aim of the Virtual High temperature Conversion Processes (VIRTUHCON) project is the theoretical modeling of high temperature conversion processes such as metallurgy and gasification. The thermodynamic properties of molten silicates (slag) are important input quantities for the modeling of phenomena in process engineering and geoscience where SiO_2 (silica) is a prime component. Although the alkaline oxides normally appear in minor quantities, they can significantly change the behavior of the slag properties because of their low melting temperatures thereby considerably lowering the liquidus temperature of the molten oxide mixture. Therefore, information on phase diagram and thermochemistry of alkaline oxide containing systems is required to help scientists in the design or development of new materials and processes. However, experimental difficulties abound in alkaline bearing systems because SiO_2 is volatile at high temperatures and alkaline oxides are difficult to handle and prone to surface hydrolysis when exposed to air. CALPHAD modeling is therefore considered a suitable choice to provide phase diagram and thermochemical information where experiments can only be performed with difficulty.

The phase diagram and thermochemical information of the K_2O-SiO_2 and Na_2O-SiO_2 systems have already been thermodynamically evaluated in the literature [1-7]. There, the liquid phase was described using the modified quasi-chemical model [8] and the modified associate species model [9]. In the present work, the ionic two-sublattice model [10-11] is applied to describe the liquid phase in these systems as this model allows an adequate representation of the thermodynamic properties for complex liquids such as slag. Furthermore, this model allows coupling a large database for oxides to simple metal systems. A detailed literature review of these two systems can be found in Ref. [11], while new assessments of the K_2O-SiO_2 and Na_2O-SiO_2 systems were recently carried out by Schmetterer et al. and Zhang et al. [12, 13].

The thermodynamic parameters of the CaO-SiO_2 system have been optimized several times [14-17]. Recently, we performed a survey of literature data for the Cp of the calciumsilicate phases [18] and made a new determination of the

Cp of Pseudowollastonite ($CaSiO_3$ – see Table 1) which was found to be in good agreement with the literature. These results were included in our thermodynamic description of this system.

However, no phase diagram and thermochemical information for the K_2O-CaO and Na_2O-CaO systems are available so that the thermodynamic descriptions of these two systems had to be based on simple extrapolations of the Gibbs energy functions of the pure oxides compounds.

Literature for the ternary systems is scarce; the key papers for experimental investigations are from Morey et al. [19] for the K_2O-CaO-SiO_2 system and Morey and Bowen [20] for the Na_2O-CaO-SiO_2. In their reports the authors provided liquidus temperatures obtained from optical inspection of samples after quenching from various temperatures and reported the existence and composition of several ternary compounds. However, the experiments were mostly confined to the SiO_2 rich part. Six ternary compounds in this CaO–K_2O–SiO_2 system, CaK_2SiO_4, $CaK_4Si_3O_9$, $CaK_8Si_{10}O_{25}$, $Ca_3K_2Si_6O_{16}$, $Ca_2K_2Si_6O_{15}$ and $Ca_2K_2Si_9O_{21}$ were reported by Morey et al. [19]. However, they did not give any structural information in their work. Toropov and Borisenko [21] and Yung et al. [22] indicted the existence of the compound $CaK_4Si_6O_{15}$ based on X-Ray studies. Recently, the possible existence of CaK_2SiO_4 was checked [23], but the evaluations of the powder diffractograms obtained after synthesis experiments clearly indicated that for a 1:1:1 bulk composition $K_2Ca_2Si_2O_7$ is the dominant potassium calcium silicate up to the melt formation. There is no thermochemical information available in this ternary system. The CaO–Na_2O–SiO_2 system had been studied first by Morey and Bowen [20] who mentioned the existence of four ternary compounds $Ca_3Na_2Si_6O_{16}$, $Ca_2Na_2Si_3O_9$, $CaNa_4Si_3O_9$, and $CaNa_2SiO_4$. Segnit [24] had obtained the new compound $Ca_3Na_8Si_5O_{17}$ and $Ca_2Na_2Si_2O_7$ in the parts of this ternary system richer in CaO and Na_2O. The compound $Ca_8Na_4Si_5O_{20}$ had been found by Toropov and Arakelyan [25]. Later, Fedorov and Brodkina [26] considered this phase to be a mixture of a solid solution with Ca_2SiO_4 and $CaNa_2SiO_4$ instead of an individual compound. The six ternary compounds from the literature were considered in this work. The phase diagram and thermochemical information is also limited in this ternary system to the work from Morey and Bowen [20]. Further experimental phase diagram data and thermodynamic properties have not been determined until now.

The goal of the present work is to describe the current knowledge about the thermodynamic properties of the M_2O-CaO-SiO_2 (M=K, Na) ternary systems which are constituents of the complex Al_2O_3-CaO-MgO-SiO_2-M_2O (M=K, Na) system. The optimization of these ternary systems is the first step in the estimation of thermodynamic properties and phase diagrams of the subsequent multicomponent systems.

2. Thermodynamic Modeling

2.1 Liquid phase

It can be assumed that Ca^{2+}, K^{+}, Na^{+}, O^{2-}, SiO_4^{4-}, SiO_2^{0} and Va^{-} exist in the liquid phase of the CaO-M_2O-SiO_2 (M=K, Na) systems, and that the electric neutrality is maintained depending on the relative amounts of positive or negative ions for a given temperature. The two-sublattice model for the ionic solution suggested by Hillert et al. [10] can be used to express the Gibbs energy of this system. This model utilizes two sublattices, one for cations and the other for anions, neutral species and vacancies. Thus, the formula unit of the CaO-M_2O-SiO_2 (M=K, Na) systems can be expressed as

$$(Ca^{+2}, M^{+1})_P (O^{-2}, SiO_4^{-4}, SiO_2^0, Va^-)_Q \quad \text{(M= K, Na)}$$

where Va^- denotes the vacancies. The indices P and Q represent the mole number of cations and anions of the two sublattices in order to maintain the electric neutrality, as described by Eqs. (1) and (2)

$$P = 2y_{O^{-2}} + 4y_{SiO_4^{-4}} \tag{1}$$

$$Q = y_{M^{+1}} + 2y_{Ca^{+2}} \tag{2}$$

Although this model yields complicated thermodynamic expressions, in practice, all calculations are carried out automatically using thermodynamic software packages such as Thermo-Calc [27]. The Gibbs energy of the liquid in this system is given by Eq. (3)

$$\begin{aligned} G_m = & \sum\sum y_i y_j {}^0G_{ij} + Q\sum y_k {}^0G_k + PRT\sum y_i \ln y_i \\ & + QRT(\sum y_j \ln y_j + \sum y_k \ln y_k) + {}^EG_m \end{aligned} \tag{3}$$

where i is a cation, Ca^{+2} or K^{+1} or Na^{+1}, j is an anion, O^{-2} or SiO_4^{-4}, and k is neutral as in SiO_2^0, ${}^EG_m$ represents excess Gibbs energy. The last term, ${}^EG_m$, can be expressed by Eq. (4)

$${}^EG_m = \sum_{v=o}^{v=s} y_i y_j y_k \sum_{v=0}^{v=n} {}^vL_{i:j,k}(y_j - y_k)^v + \sum_{v=o}^{v=n} y_i y_j y_k y_l L_{i,j:k,l}(y_i - y_j)(y_k - y_l) \tag{4}$$

where i, j, k and l is a cation or anion or neutral as in SiO_2^0. $L_{i:j,k}$ and $L_{i,j:k,l}$ are the interaction parameters between two sub-lattices that were optimized in this work.

2.2 Solid phases

In the CALPHAD technique, the thermodynamic properties of each solid phase are represented by the parameters S_{298} (the entropy of the solid at 298.15 K), $Cp(T)$ (the heat capacity of the solid) and ΔH_{298} ,(the change in enthalpy of the solid) where

$$C_p = a + bT + cT^{-2} \tag{5}$$

The Gibbs energy values are given in relation to the enthalpy of selected reference states for the elements at 298.15 K according to Eq. (6). This state is denoted by SER (Stable Element Reference)

$${}^0G - H^{SER} = A + B/T + CT + DT\ln T + ET^2 + \ldots \tag{6}$$

with the parameters A, B, C, D and E being optimized, i.e. determined in such a way that the calculated phase diagram matches the experimental information.

In the current work, the Gibbs functions of three compounds $K_2Ca_2Si_2O_7$ and $K_8CaSi_{10}O_{25}$ were based on our own heat capacity data from drop calorimetry [28]. The thermodynamic parameters of other compounds were assessed based on the phase relations from the work of Morey et al. [19]. So far, the interpretation of the results concerning the existence and formation of certain phases had to rely exclusively on the only available phase equilibrium study of the K_2O-CaO-SiO_2 ternary system that was published 80 years ago by Morey et al. [19].The optimization of the CaO-M_2O-SiO_2 (M=K, Na) systems was carried out using the Thermo-Calc software [27]. This module works by minimizing the square sum of the differences between experimental and calculated values. In the optimization procedure, each set of experimental data was given a certain weight. The weights were changed systematically during the optimization until most of the experimental data could be accounted for within the claimed uncertainty limits.

The parameters for the liquid phase were first optimized using the experimental liquidus temperatures. The thermodynamic parameters of the solid compounds were assessed next by using the phase diagram data and the heat capacities. All of the parameters were finally evaluated together to give a reasonable description of these systems.

The thermodynamic parameters from the optimization are listed in Table 1 below.

Table 1 Thermodynamic parameters of CaO-SiO_2-M_2O (M=K, Na) systems

Phase	Thermodynamic Parameters (J/mol)
$Ca_2K_2Si_2O_7$	$G_{Ca2K2Si2O7} = \text{-}4\times10^6 + 1878.85T - 296.52202T\ln T - 0.0213315T^2 + 1447659.99T^{-1}$
$CaK_4Si_3O_9$	$G_{CaK4Si3O9} = \text{-}3.73\times10^5 + 10T + 2GK2O + 3GSIO2 + GCAO$
$CaK_8Si_{10}O_{25}$	$G_{Ca2K2Si2O7} = \text{-}5733236.456 + 1475.356T - 1049T\ln T - 9.6487\times10^6 T^{-1}$
$CaK_4Si_6O_{15}$	$G_{CaK4Si6O15} = \text{-}3.93\times10^5 + 9.005T + 2GK2O + 6GSIO2 + GCAO$
$Ca_3K_2Si_6O_{16}$	$G_{Ca3K2Si6O16} = \text{-}4.65\times10^5 + 8.04T + GK2O + 6GSIO2 + 3GCAO$
$Ca_2K_2Si_6O_{15}$	$G_{Ca2K2Si6O15} = \text{-}3.704\times10^5 + 10.01T + GK2O + 6GSIO2 + 2GCAO$
$Ca_2K_2Si_9O_{21}$	$G_{Ca2K2Si9O21} = \text{-}3.72\times10^5 + 10.01T + GK2O + 9GSIO2 + 2GCAO$
$CaNa_2SiO_4$	$G_{CaNa2SiO4} = \text{-}2.2015\times10^5 + 48.85T + GNA2O + GSIO2 + GCAO$
$Ca_3Na_8Si_5O_{17}$	$G_{Ca3Na8Si5O17} = \text{-}4.93015\times10^5 + 70.0025T + 4GNA2O + 5GSIO2 + 3GCAO$
$Ca_2Na_2Si_2O_7$	$G_{Ca2Na2Si2O7} = \text{-}3.40009\times10^5 + 64.0018T + GNA2O + 2GSIO2 + 2GCAO$
$Ca_2Na_2Si_3O_9$	$G_{Ca2Na2Si3O9} = \text{-}3.98009\times10^5 + 70.0018T + GNA2O + 3GSIO2 + 2GCAO$
$CaNa_4Si_3O_9$	$G_{CaNa4Si3O9} = \text{-}4.54\times10^5 + 108.037T + 2GNA2O + 3GSIO2 + GCAO$
$Ca_3Na_2Si_6O_{16}$	$G_{Ca3Na2Si6O16} = \text{-}4.904\times10^5 + 70T + GNA2O + 6GSIO2 + 3GCAO$

3. Results and Discussions

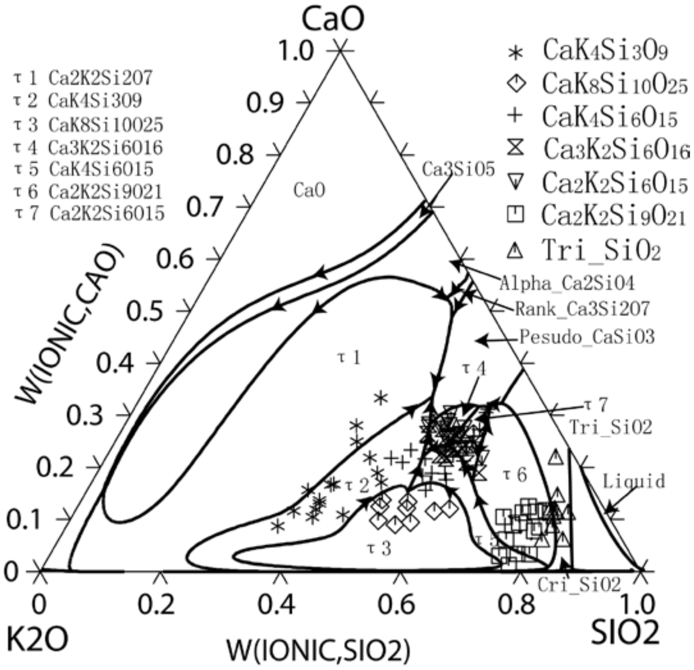

Fig. 1 Calculated phase diagram of CaO-K_2O-SiO_2 system

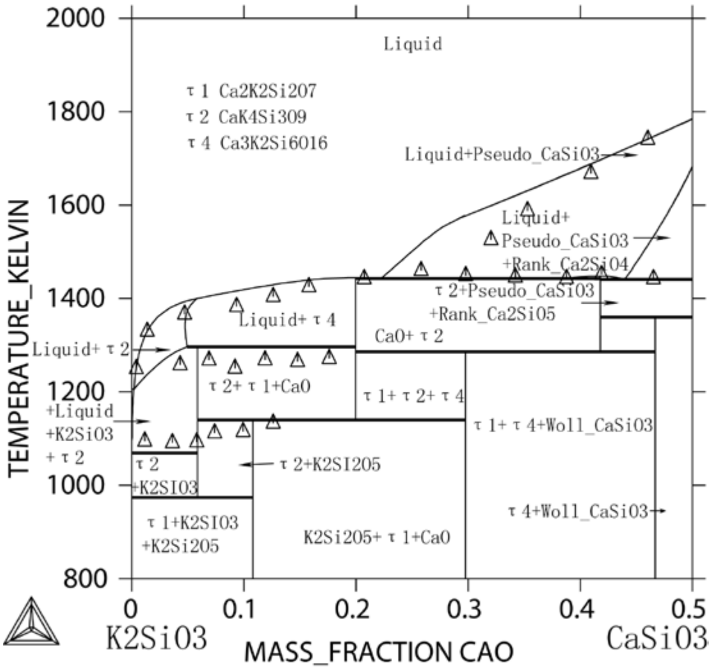

Fig. 2 Calculated vertical section (K_2SiO_3-$CaSiO_3$) with experimental results [19]

Seven ternary compounds were included in the CaO-K_2O-SiO_2 system. The Cp data from our own measurement for the compounds $K_2Ca_2Si_2O_7$ and $K_8CaSi_{10}O_{25}$ were considered in this optimization. The calculated liquidus temperatures are shown in Fig. 1, which is in good agreement with the experimental results from Morey et al. [19] in the respective composition range. It has, however, to be noted that the K_2O-rich part is extrapolated and not supported by experimental data. Comparing our calculated results with the experimental results, it can be found that there are differences between the experimental data [19] and the calculated results close to the compound $CaK_4Si_6O_{15}$. This region still needs experimental attention and further optimization.

A calculated vertical section (K_2SiO_3-$CaSiO_3$) of the CaO-K_2O-SiO_2 ternary system is given in Fig. 2. Again it can be seen that the agreement between the present calculation and the measurement is good. The calculated liquidus surface of the CaO-Na_2O-SiO_2 system is shown in Fig. 3 together with the primary crystallization fields. The six ternary compounds reported in the literature were included in the calculation. Figure 4 shows the calculated isothermal section at 2000 K, where the liquid miscibility gap close to the SiO_2 corner extends into the ternary system. With increasing temperature the boundary of the miscibility gap will shift toward the CaO-SiO_2 binary system. The calculated invariant reactions on this system were shown in Table 3. The isothermal section at 1273 K is given in Fig. 5, where five ternary compounds, $Ca_2Na_2Si_2O_7$, $CaNa_2SiO_4$, $Ca_2Na_2Si_3O_9$, $CaNa_4Si_4O_9$, $Ca_3Na_2Si_6O_{16}$, are stable. The calculated vertical section (Na_2SiO_4-$CaSiO_3$) of this ternary system is given in Fig. 6 and shows good agreement between the present calculation and the measurements [20].

Table 3 Invariant reactions of CaO-SiO_2-M_2O (M=K, Na) systems

Reaction	Type	T/K	Ref
L+$Ca_2K_2Si_2O_7$ $\Leftrightarrow$ Pesudo_$CaSiO_3$+$CaK_4Si_3O_9$	U	1073	[19]
		1061	This work
L $\Leftrightarrow$ Pesudo_$CaSiO_3$+$CaK_4Si_3O_9$+$Ca_3K_2Si_6O_{16}$	E	1050	[19]
		1049	This work
L+ Pesudo_$CaSiO_3$+ $Ca_2K_2Si_6O_{15}$ $\Leftrightarrow$ $Ca_3K_2Si_6O_{16}$	P	1273	[19]
		1257	This work
L+$CaK_8Si_{10}O_{25}$ $\Leftrightarrow$ $CaK_4Si_3O_9$+$CaK_4Si_6O_{15}$	U	1170	[19]
		1157	This work
L+$Ca_2K_2Si_9O_{21}$ $\Leftrightarrow$ $Ca_2K_2Si_6O_{15}$+$CaK_4Si_6O_{15}$	U	1098	[19]
		1065	This work
L+$Ca_2K_2Si_6O_{15}$ $\Leftrightarrow$ $Ca_3K_2Si_6O_{16}$+$CaK_4Si_6O_{15}$	U	1223	[19]
		1234	This work
L+ Pesudo_$CaSiO_3$ $\Leftrightarrow$ $Ca_3Na_2Si_6O_{16}$+Tri_SiO_2	U	1323	[20]
		1354	This work
L+$Ca_2Na_2Si_2O_7$ $\Leftrightarrow$ $Ca_3Na_2Si_6O_{16}$+$Ca_2Na_2Si_3O_9$	U	1423	[20]
		1417	This work
L+$Ca_3Na_2Si_6O_{16}$+$Ca_2Na_2Si_3O_9$ $\Leftrightarrow$ $CaNa_4Si_3O_9$	P	1157	[20]
		1170	This work

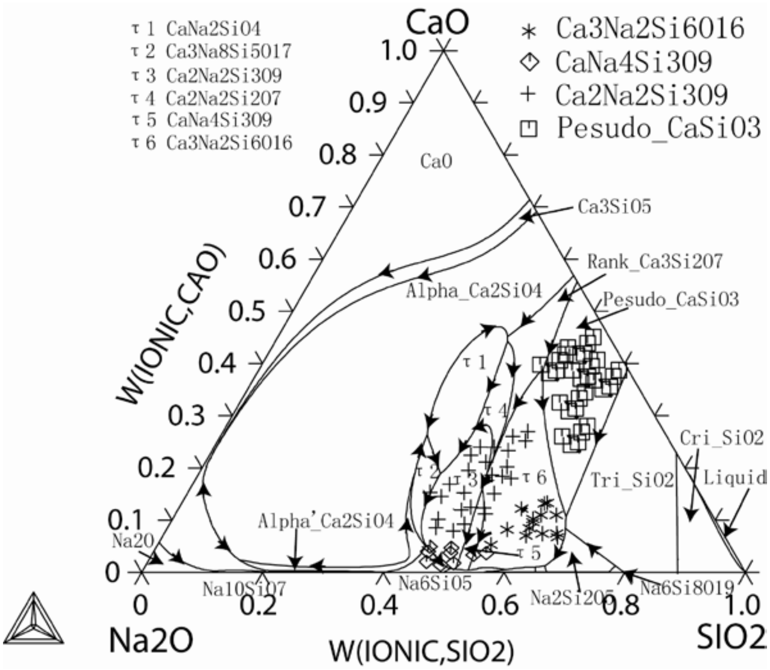

Fig. 3 Calculated phase diagram of CaO-Na_2O-SiO_2 system

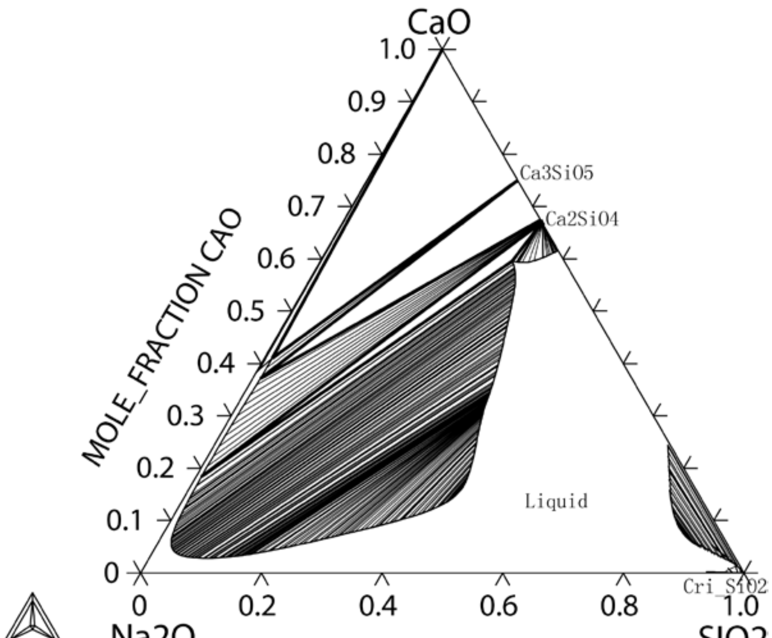

Fig. 4 Calculated isothermal section at 2000 K in CaO-Na_2O-SiO_2 system

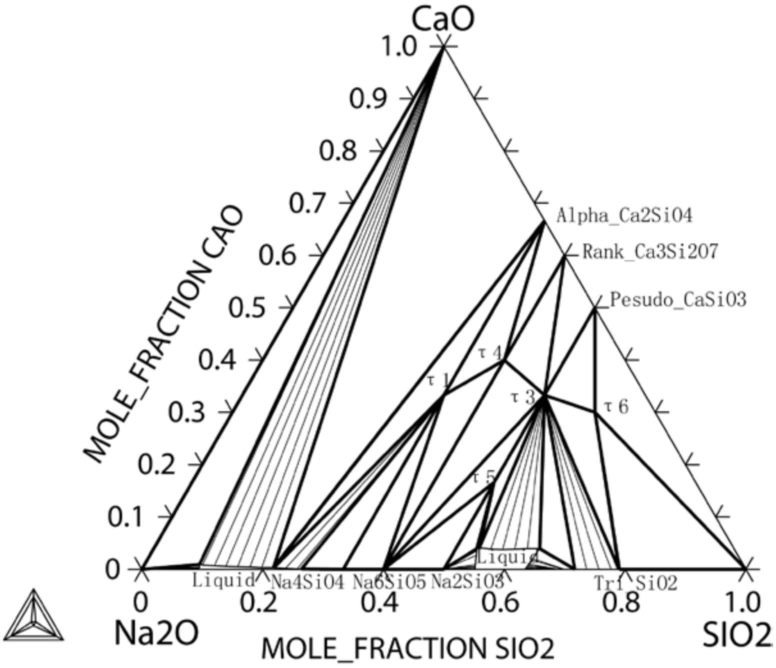

Fig. 5 Calculated isothermal section at 1273 K

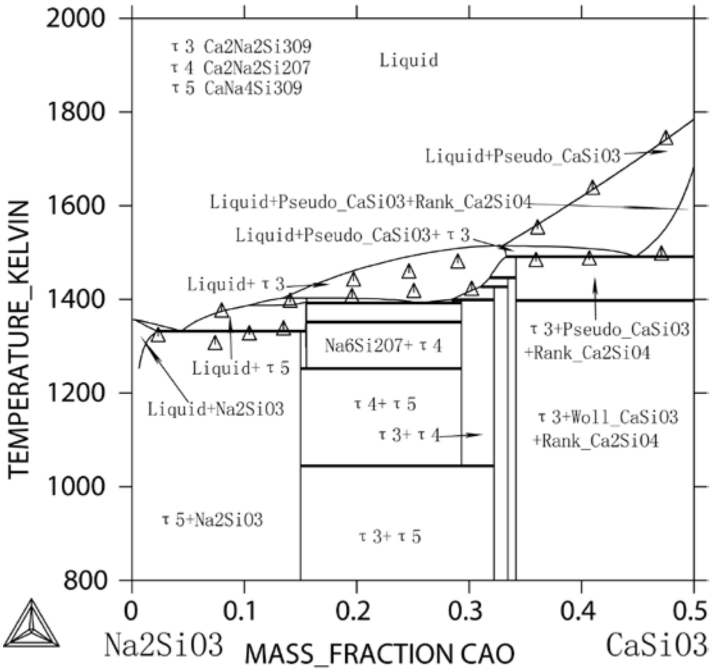

Fig. 6 Calculated vertical section (Na_2SiO_3-$CaSiO_3$)

4. Conclusions

Based on the previous assessments and our own optimization of the sub-binary systems, the thermodynamic properties and phase equilibria of the CaO-M_2O-SiO_2 (M=K, Na) systems have been assessed. The two-sublattice model for ionic solutions can be used to describe these two ternary systems. In addition, the experimentally determined heat capacities of three solid compounds were included in the dataset. Reasonable agreement between calculated and experimental data has been achieved.

Nevertheless, the need of more experimental information for the phase diagrams and thermodynamic properties is desirable in order to have more detailed and confident phase diagram description. Experimental work in the CaO-M_2O-SiO_2 (M=K, Na) systems is therefore strongly encouraged.

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